International Journal of Thermophysics, Vol. 21, No. 5, 2000

New Universal Relations for Liquid-Vapor Phase Equilibrium

V. P. Skripov[1, 2] and M. Z. Faizullin[1]

Received February 22, 1999

Universal relations between the saturation pressure p_{LV} and the value of $\varphi = \Delta h_{LV}/\Delta v_{LV} - p_{LV}$, where Δh_{LV} is the latent heat of evaporation and Δv_{LV} is the volume change of the vapor-liquid transition, and the product of the orthobaric densities ρ_L and ρ_V of the liquid and vapor at coexistence have been discovered. In the temperature range from the triple point to $T/T_c \approx 0.9$, these relations obey a power law with universal exponents. At temperatures $0.9 < T/T_c \leqslant 1$, p_{LV} and φ depend linearly on $\ln(\rho_L \rho_V)$ with retention of universality for substances of different nature.

KEY WORDS: heat of evaporation; orthobaric densities; saturation pressure; universal relation; vapor-liquid phase equilibrium.

1. INTRODUCTION

The pressure p_{LV} of a pure substance at a liquid(L)-vapor(V) phase equilibrium is only a function of the temperature, $p_{LV} = f(T)$, but this relationship has a complicated form. One can use, for example, the following approximation [1],

$$\log p_{LV} = A + BT^{-1} + C \log T + DT^6 \tag{1}$$

where A, B, C, and D are system-dependent coefficients. In polynomials of type (1), the main term BT^{-1} with $B < 0$ corresponds to an integration of the Clausius–Clapeyron equation at constant evaporation enthalpy Δh_{LV} and with substitution of $\Delta v_{LV} = v_V - v_L \approx v_V = RT/p_{LV}$, where v_{LV} represents the molar volume of the vapor and liquid phase at coexistence.

---

[1] Institute of Thermal Physics, Russian Academy of Sciences, Ural Branch, GSP-828, Pervomaiskaya 91, Ekaterinburg 620219, Russia.

[2] To whom correspondence should be addressed.

0195-928X/00/0900-1213$18.00/0

One could assume the existence of an indirect simple relation of the form $p_{LV} = \varphi[x(T)]$, where x is one of the properties of a two-phase system in equilibrium. For this purpose, the Van der Waals equation proved to be useful:

$$p = \frac{RT}{v-b} - \frac{a}{v^2} \tag{2}$$

For a fluid with such an equation of state the molar internal energy u and the entropy s can be written as [2]

$$u = c_V T - \frac{a}{v} \tag{3}$$

$$s = c_V \ln T + R \ln(v-b) \tag{4}$$

where c_V is the molar isochoric heat capacity.

Equations (3) and (4) make it possible to obtain the chemical potential $\mu = u - Ts + pv$. The condition of phase equilibrium

$$\mu_L(T, p) = \mu_V(T, p) \tag{5}$$

leads to a dependence of the equilibrium pressure p_{LV} on the temperature and the specific volumes v_L of the liquid and v_V of the vapor on the saturation curve:

$$p_{LV} = \frac{RT}{v_V - v_L} \ln \frac{v_V - b}{v_L - b} - \frac{a}{v_L v_V} \tag{6}$$

By making simple transformations in Eq. (6) and with the orthobaric densities, $\rho_L = 1/v_L$ and $\rho_V = 1/v_V$, we obtain

$$p_{LV} = a\rho_L \rho_V \left\{ \frac{RT}{a} \frac{\ln(\rho_L/\rho_V) + \ln[(1-b\rho_V)/(1-b\rho_L)]}{\rho_L - \rho_V} - 1 \right\} \tag{7}$$

The structure of Eq. (7) shows that for the Van der Waals equation the saturation pressure is mainly determined by the value of $a\rho_L \rho_V$, i.e., the product of the orthobaric densities of the liquid and vapor. If we use experimental data for different substances, we find that the product $T(\ln(\rho_L/\rho_V) + \ln[(1-b\rho_V)/(1-b\rho_L)])/(\rho_L - \rho_V)$ in the range from the triple point to the critical point varies only slightly; for example, for nitrogen by 13%, for carbon dioxide by 14%, for mercury by 5%, whereas the product $\rho_L \rho_V$ increases by four orders of magnitude.

2. RELATION BETWEEN SATURATION PRESSURE AND ORTHOBARIC DENSITIES

Having obtained an interesting result for the Van der Waals fluid, we decided to verify whether the relation $p_{\mathrm{LV}} = f(\rho_{\mathrm{L}} \rho_{\mathrm{V}})$ applies in a general sense. For this purpose we considered experimental data for the saturated vapor pressure p_{LV} and the orthobaric densities ρ_{L} and ρ_{V} of a large group of substances. It turns out that a power law of the form

$$p_{\mathrm{LV}} = A(\rho_{\mathrm{L}} \rho_{\mathrm{V}})^n \tag{8}$$

with $n \approx 1.1$ adequately approximates the experimental data in the temperature range from the triple point to $T/T_{\mathrm{c}} \approx 0.9$, where T_{c} is the critical temperature. In terms of pressure the upper boundary of the range corresponds to $p/p_{\mathrm{c}} = 0.5$, where p_{c} is the critical pressure. Figure 1 shows on a logarithmic scale the relation between the saturation pressure and the product $\rho_{\mathrm{L}} \rho_{\mathrm{V}}$ for water and mercury at various temperatures. Deviations from linearity in Fig. 1 are observed only in the vicinity of the critical point.

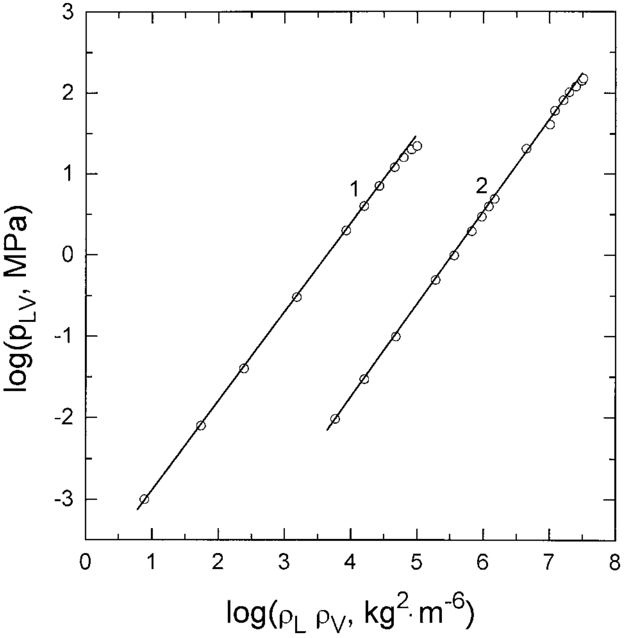

Fig. 1. Saturation pressure p_{LV} as a function of the product of liquid and vapor densities $\rho_{\mathrm{L}} \rho_{\mathrm{V}}$ at coexistence: 1, water; 2, mercury.

To bring the power law expressed by Eq. (8) into a universal form, we introduce quantities reduced in terms of the critical parameters p_c, T_c, ρ_c:

$$\tilde{p}_{\mathrm{LV}} = p_{\mathrm{LV}}/p_c, \qquad \tilde{\rho}_{\mathrm{L}} = \rho_{\mathrm{L}}/\rho_c, \qquad \text{and} \qquad \tilde{\rho}_{\mathrm{V}} = \rho_{\mathrm{V}}/\rho_c$$

and rewrite Eq. (8) as

$$\tilde{p}_{\mathrm{LV}} = \tilde{A}(\tilde{\rho}_{\mathrm{L}}\tilde{\rho}_{\mathrm{V}})^n, \qquad \text{where} \quad \tilde{A} = A p_c^{-1}\rho_c^{2n} \tag{9}$$

Figure 2 shows data for substances of different nature in dimensionless variables. Values of n, $\tilde{A}$ for these substances obtained with the use of the method of least squares are presented in Table I. Figure 2 and Table I elucidate the universality of the relation between the product of orthobaric densities and the saturation pressure over a wide temperature range. For Eq. (9) one can assume, in general that, $n = 1.13 \pm 0.02$, $\tilde{A} = 1.3 \pm 0.1$.

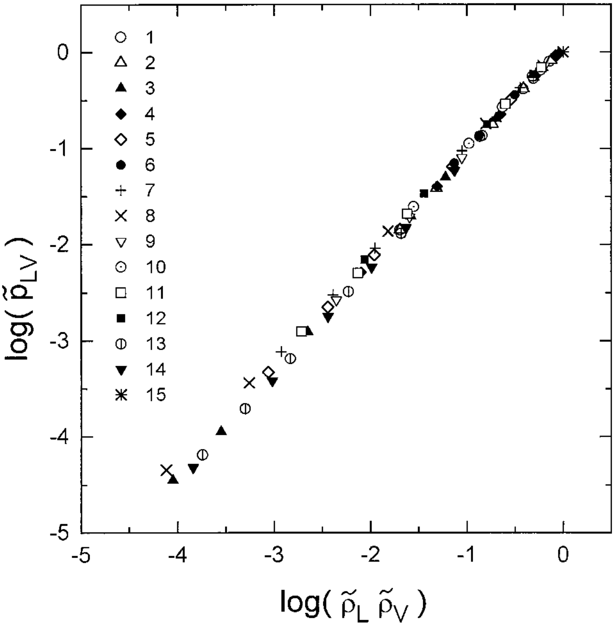

Fig. 2. Reduced pressure $\tilde{p}_{\mathrm{LV}}$ on the saturation line as a function of the value of $\tilde{\rho}_{\mathrm{L}}\tilde{\rho}_{\mathrm{V}}$ for different substances: 1, argon; 2, xenon; 3, oxygen; 4, nitrogen; 5, chlorine; 6, carbon dioxide; 7, ammonia; 8, water; 9, methane; 10, hexane; 11, benzene; 12, diethyl ether; 13, mercury; 14, cesium; 15, critical point.

Table I. Values of the Parameters in Eqs. (9) and (14)

Substance	n	$\tilde{A}$	k	D^*	Ref.
Argon	1.15	1.25	0.97	0.98	[3]
Xenon	1.14	1.23	0.97	1.00	[3]
Oxygen	1.13	1.23	0.99	0.98	[6]
Nitrogen	1.13	1.23	0.97	0.99	[7]
Chlorine	1.13	1.30	0.98	0.98	[4]
Carbon dioxide	1.12	1.31	0.95	1.00	[4]
Ammonia	1.12	1.38	0.98	0.97	[4]
Water	1.10	1.33	0.97	0.98	[8]
Methane	1.14	1.25	0.98	1.01	[9]
Hexane	1.11	1.34	0.97	1.01	[4]
Benzene	1.14	1.40	0.97	0.99	[4]
Diethyl ether	1.11	1.35	0.96	1.01	[4]
Mercury	1.14	1.13	0.99	—	[4, 5]
Cesium	1.14	1.09	1.00	0.99	[10]

As we approach the critical point, the character of the relation changes, but its universality is retained. In the range $0.9 < \tilde{T} \leqslant 1$, where $\tilde{T} = T/T_c$, the experimental data can be represented by

$$p_{LV} = B \ln(\rho_L \rho_V) + C \tag{10}$$

or in terms of dimensionless variables,

$$\tilde{p}_{LV} = \ln(\tilde{\rho}_L \tilde{\rho}_V)^m + 1 \tag{11}$$

with $m = 0.65$. We note as a curious observation that the exponent m is close to twice the value of the critical exponent β for the asymptotic power law of the coexisting densities. Figure 3 shows this relation for a number of substances.

Equations (8)–(11) refer to thermal properties of substances at two-phase liquid-vapor equilibrium. We suggest that they should be called multiplicative relations as on the right-hand side of the equalities there is a product of the orthobaric densities of the two phases.

3. RELATION WITH CALORIC PROPERTIES

The question arises whether it is possible to present the behavior of caloric quantities, such as, the entropy change $\Delta s_{LV} = s_V - s_L$, the enthalpy change $\Delta h_{LV} = h_V - h_L = T\,\Delta s_{LV}$, or the internal energy change $\Delta u_{LV} = \Delta h_{LV} - p_{LV}\,\Delta v_{LV}$, similarly as a function of the product $\rho_L \rho_V$.

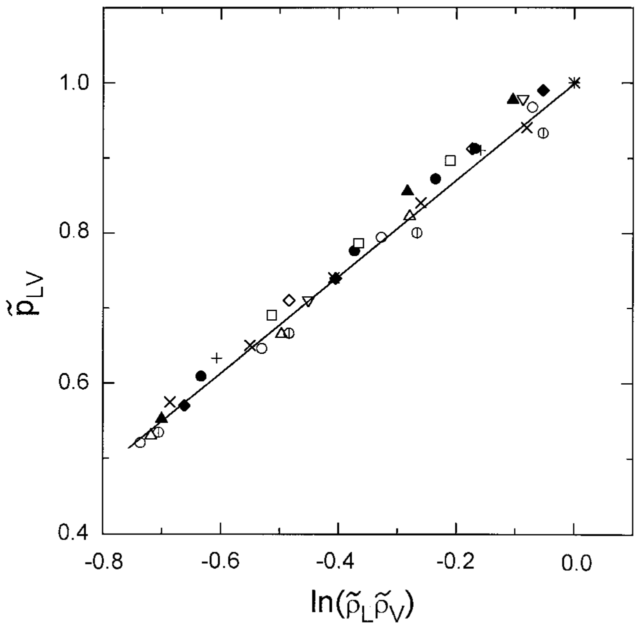

Fig. 3. Reduced pressure $\tilde{p}_{LV}$ on the saturation line as a function of the value of $\tilde{\rho}_L\tilde{\rho}_V$ for various substances in the range $0.9 < \tilde{T} \leqslant 1$. The symbols are the same as in Fig. 2. The solid line represents Eq. (11).

One can again obtain a useful indication by turning to the Van der Waals equation. If we introduce the entropy, given by Eq. (4), into the condition of phase equilibrium, given by Eq. (5), and take into account the independence of the heat capacity on the volume, we obtain

$$p_{LV} = T\,\frac{\Delta s_{LV}}{\Delta v_{LV}} - a\rho_L\rho_V$$

or

$$\frac{\Delta h_{LV}}{\Delta v_{LV}} - p_{LV} = a\rho_L\rho_V \qquad (12)$$

$$\frac{\Delta u_{LV}}{\Delta v_{LV}} = a\rho_L\rho_V$$

The clue is the fact that for the Van der Waals fluid the value of

$$\varphi = \frac{\Delta h_{\mathrm{LV}}}{\Delta v_{\mathrm{LV}}} - p_{\mathrm{LV}} \tag{13}$$

is proportional to the product $\rho_{\mathrm{L}} \rho_{\mathrm{V}}$. We have calculated the values of φ and of $\rho_{\mathrm{L}} \rho_{\mathrm{V}}$ for a number of substances over a wide temperature range from vapor-liquid equilibrium data. Assuming in the general case a power law of the form:

$$\varphi = D(\rho_{\mathrm{L}} \rho_{\mathrm{V}})^k \tag{14}$$

we have plotted them on a logarithmic scale. Figure 4 presents such a construction for water, cesium, argon, and mercury. In all cases the points fall on a straight line with a slope $k \approx 1$ for $T/T_{\mathrm{c}} \leqslant 0.9$.

It is convenient to make a transition to dimensionless variables in Eqs. (13) and (14) by considering a certain reference point on the saturation line. We have chosen the point $p_1 = 0.1 p_{\mathrm{c}}$. Figure 5 shows experimental

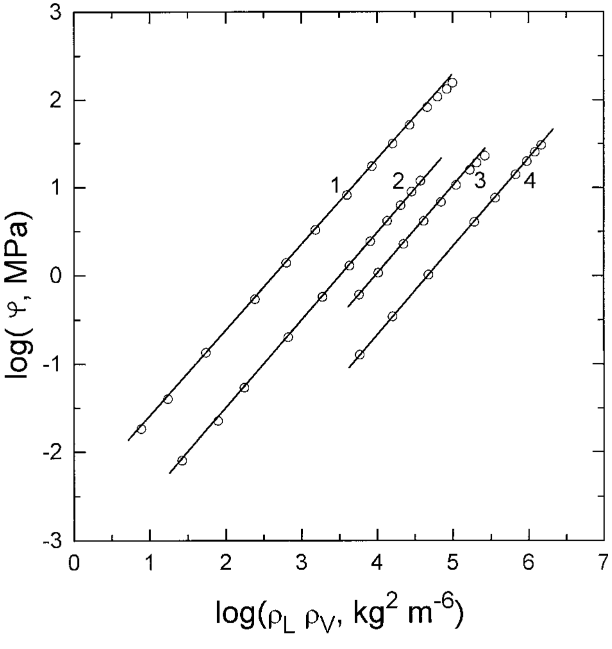

Fig. 4. The value of $\varphi = \Delta h_{\mathrm{LV}}/\Delta v_{\mathrm{LV}} - p_{\mathrm{LV}}$ as a function of the product of liquid and vapor densities at coexistence: 1, water; 2, cesium; 3, argon; 4, mercury.

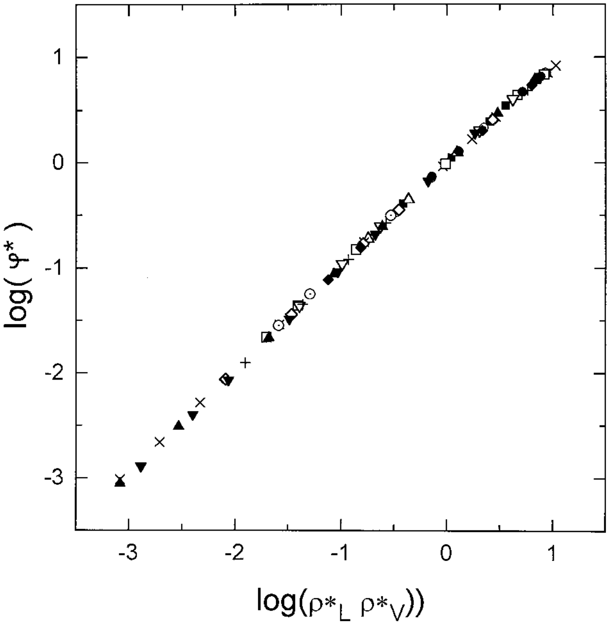

Fig. 5. Reduced value of φ^* on the saturation line as a function of $\rho_\mathrm{L}^*\rho_\mathrm{V}^*=(\rho_\mathrm{L}\rho_\mathrm{V})/(\rho_\mathrm{L}\rho_\mathrm{V})_1$ for various substances. The symbols are the same as in Fig. 2.

values $\rho_\mathrm{L}^*\rho_\mathrm{V}^*=(\rho_\mathrm{L}\rho_\mathrm{V})/(\rho_\mathrm{L}\rho_\mathrm{V})_1$, $\varphi^*=\varphi/\varphi_1$ for the same substances as those in Fig. 2 except mercury. Indeed, the universality of the multiplicative relationship, Eq. (14), for the quantities $\Delta h_\mathrm{LV}/\Delta v_\mathrm{LV}$, $\Delta u_\mathrm{LV}/\Delta v_\mathrm{LV}$ with the exponent $k=1.0$ and amplitude $D^*=1.0$, where $D^*=D\varphi_1^{-1}(\rho_\mathrm{L}\rho_\mathrm{V})_1^k$, is confirmed. Closer to the critical point, in the range $0.9<\tilde{T}\leqslant 1$, the relation between φ^* and $\rho_\mathrm{L}^*\rho_\mathrm{V}^*$ may be described as

$$\varphi^*=\ln(\rho_\mathrm{L}^*\rho_\mathrm{V}^*)^r-2.5 \tag{15}$$

at $r=4.3$. The behavior of this relationship for various substances is shown in Fig. 6. As is evident from the figure, in the range $0.9<\tilde{T}\leqslant 1$ one can observe retention of universality in the behavior of $\varphi^*(\rho_\mathrm{L}^*\rho_\mathrm{V}^*)$. The scatter of points at $T\to T_\mathrm{c}$ may be explained by the large uncertainty in the determination of the ratio $\Delta h_\mathrm{LV}/\Delta v_\mathrm{LV}$ in Eq. (13) in the immediate vicinity of T_c. For comparison of Figs. 5 and 6 one should bear in mind the difference in scales along the abscissa axis.

Our study has revealed simple universal relations, Eqs. (8) and (14), between the saturation pressure or the ratio $\Delta h_\mathrm{LV}/\Delta v_\mathrm{LV}$ on the one hand

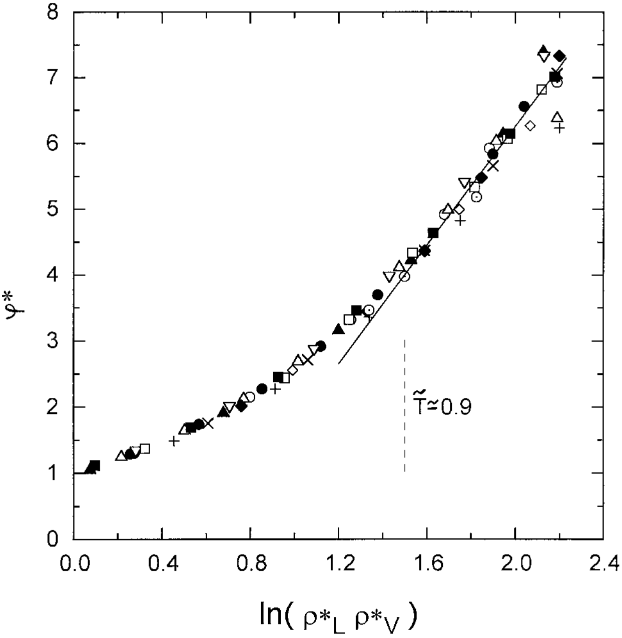

Fig. 6. Relationship between the values of φ^* and $\rho^*_L \rho^*_V = (\rho_L \rho_V)/(\rho_L \rho_V)_1$ for various substances in the vicinity of the critical point. The symbols are the same as in Fig. 2. The solid line represents Eq. (15).

and the product of orthobaric densities of coexistent phases on the other hand. The function φ, defined by Eq. (13), may be presented in an equivalent form $\varphi = T(\Delta s_{LV}/\Delta v_{LV}) - p_{LV} = \Delta u_{LV}/\Delta v_{LV}$. The other form of φ may be obtained if we use the Clausius–Clapeyron equation $dp/dT = \Delta s/\Delta v$. In this case we can write

$$\varphi = T\left(\frac{dp}{dT}\right)_{LV} - p_{LV} \tag{16}$$

4. CONCLUSION

The universal relations elucidated in this paper can be used to evaluate the product of orthobaric densities if the vapor pressure is known or to evaluate the evaporation enthalpy by orthobaric densities on the saturation line. Of course, a comprehensive quantitative comparison of the properties of various substances with established correlations is still to be done. This will make it possible, if necessary, to introduce certain corrections taking into account subtle individual differences in thermodynamic properties of substances. But, in essence, this problem requires additional investigation.

It may be assumed that the revealed universality is caused by the very nature of a system with a large number of interacting particles (molecules) with attractive and repulsive forces between them. This is supported by the fact that even a simple allowance for these forces that is contained in the Van der Waals equation results in a distinct relation between p_{LV}, Δh_{LV} and the product $\rho_{\mathrm{L}} \rho_{\mathrm{V}}$. It should be noted that in Eq. (2) the quantity a/v^2 has the meaning of the internal pressure of a fluid, therefore $a/v_{\mathrm{L}} v_{\mathrm{V}}$ may be called the effective internal pressure in phase equilibrium.

REFERENCES

1. R. C. Reid, J. M. Prausnitz, and T. K. Sherwood, *The Properties of Gases and Liquids* (McCraw–Hill, New York, 1977).
2. E. Fermi, *Thermodynamics* (Prentice–Hall, New York, 1937), pp. 65–70.
3. V. A. Rabinovich, A. A. Vasserman, V. I. Nedostup, and L. S. Veksler, *Thermal Properties of Neon, Argon, Krypton and Xenon* (Izdatelstvo Standartov, Moscow, 1976), pp. 408–411.
4. N. B. Vargaftic, *Thermal Properties of Gases and Liquids* (Fizmatgiz, Moscow, 1963), p. 446.
5. I. K. Kikoin and A. P. Senchenkov, *Fiz. Metallov Metalloved* **24**:843 (1967) [in Russian].
6. V. V. Sychev, A. A. Vasserman, A. D. Kozlov, G. A. Spiridonov, and V. A. Tsimarny, *Thermodynamic Properties of Oxygen* (Izdatelstvo Standartov, Moscow, 1981), pp. 95–99.
7. V. V. Sychev, A. A. Vasserman, A. D. Kozlov, G. A. Spiridonov, and V. A. Tsimarny, *Thermodynamic Properties of Nitrogen* (Izdatelstvo Standartov, Moscow, 1977), pp. 138–140.
8. K. Schefler, J. Straub, and U. Grigull, *Wasserdampftafeln* (Springer-Verlag, Berlin/Heidelberg/New York, 1981), pp. 64–65.
9. V. V. Sychev, A. A. Vasserman, V. A. Zagoruchenko, A. D. Kozlov, G. A. Spiridonov, and V. A. Tsimarny, *Thermodynamic Properties of Methane* (Izdatelstvo Standartov, Moscow, 1979), pp. 154–158.
10. E. E. Shpilrain, K. A. Yakimovich, E. E. Totsky, D. L. Timrot, and V. A. Fomin, *Thermal Properties of Alkali Metals* (Izdatelstvo Standartov, Moscow, 1970), pp. 448–449.